THE SILICO-PHOSPHATE TSANGPOITE AND MATHYITE PROVIDE NEW CONSTRAINTS TO THE METASOMATIC PROCESS IN THE ANGRITE D’ORBIGNY. Hwang S-L\(^1\), Shen P\(^2\), Chu H-T\(^3\), Yui T-F\(^4\), Iizuka Y\(^5\) and Varela M.E\(^6\). \(^1\)Department of Materials Science and Engineering, National Dong Hwa University, Hualien, Taiwan, ROC; \(^2\)Department of Materials and Optoelectronic Science, National Sun Yat-sen University, Kaohsiung, Taiwan, ROC; \(^3\)Central Geological Survey, PO Box 968, Taipei, Taiwan, ROC; \(^4\)Institute of Earth Sciences, Academia Sinica, Taipei, Taiwan, ROC; \(^5\)Instituto de Ciencias Astronómicas de la Tierra y del Espacio (ICATE) Avenida España 1512 sur, J5402DSP, San Juan, Argentina.

**Introduction:** Tsangpoite, ideally Ca\(_5\)(PO\(_4\))\(_2\)SiO\(_4\), the hexagonal polymorph of silicocarnotite (IMA 2014-110, [1]), and matyhte, ideally (Ca\(_{10}\)(Ca\(_{2}\)Fe\(_{3}\)O\(_{10}\))Fe\(_2\)P\(_4\)O\(_{10}\)), the Fe-analogue of Ca-merrillite (IMA 2015-121, [2]), were identified in the D’Orbigny angrite meteorite. The study of these two new phosphates – previously described as silica-phosphate in the angrite D’Orbigny [3-4] – help to advance in the comprehension of the metasomatic processes which led to enrichments in FeO and MnO that highly modify the Mg-rich composition of the olivines to the one seen now [5].

**Samples and analytical techniques:** Two polished slab samples: D’Orbigny C-N1172-NH and M1173 (Naturhistorisches Museum Wien, Austria) belong to the porous part and the dense part of the angrite D’Orbigny, respectively. Samples were studied by optical microscopy and SEM-BEI imaging and energy-dispersive X-ray (SEM-EDX) techniques. Analyses were done using a JEOL JSM-7000F field emission scanning electron microscope. TEM samples were prepared by the FIB technique (using a SEIKO SMI-3050) for selected area electron diffraction (SAED) using a JEOL 3010 AEM.

**Textural setting:** Tsangpoite and matyhte specifically occur in well-defined but separated domains. Tsangpoite crystals either occur within “intact” Fe-sulfide (Fig. 1 a-b) or Fa-Kir symplectite after Fe-sulfide, or are currently embedded within the hedenbergite domain close to resorbed Fe-sulfide (Fig. 1 c). In the “intact” Fe-sulfide not in direct contact with hedenbergite, tsangpoite crystals with hexagonal cross-section occur exclusively in the local domain subjected to metasomatic replacement of Fe-sulfide by Mag + wüstit + Ts + celsian ± Al-Ti-Fe Spsl (Fig. 1 a-b).

Matyhte was not found in the “intact” Fe-sulfide but are frequently nucleated/grew within the Fe-sulfide-mediated Fa-Kir symplectite (Fig. 2a-d), yielding the occurrences of dendritic matyhte enclosed within Fa-Kir symplectite (Fig. 2b). Matyhte with high abundance of tiny Fe-sulfide droplets frequently occurs at the areas of contact between Fa-Kir symplectite and hedenbergite (Fig. 2 e-f), or between Fa-Kir overgrowth and hedenbergite.

The tsangpoite crystals that nucleated from Fe-sulfide frequently possess a central tube filled with opaque minerals (e.g. Fig. 3).

**Discussion:** Based on detailed petrographic studies these new minerals likely represent metasomatic products of an external Ca-Ti-Al-P-O rich source [6]. Accordingly and based on the petrogenetic relationships, the formation sequence likely is tsangpoite→matyhte→kuratite→Fa+Kir symplectite (over resorbed Fe-sulfide)→hedenbergite, with a crystallization temperature >1000°C. Tsangpoite is the quenched product of the high-temperature hexagonal silicocarnotite form above 1450°C in Ca\(_5\)SiO\(_4\) - Ca\(_5\)(PO\(_4\))\(_2\) system [2]. Such high temperatures are higher than the 1250°C at which a rock with the bulk composition of D’Orbigny is completely melt. Therefore, the hexagonal structure of tsangpoite could have been stabilized by vacancies (~7% cationic vacancy in the M-site) and impurities and grow at temperatures not lower than 1200°C [6]. A recent study of the silicophosphates in D’Orbigny [7] showed that the water content estimated from raw counts on \(^1\)H range from 85 to 1892 \(\mu\)g g\(^{-1}\). Although these water contents are considered as approximation [7] they seem to be at odd with the lack of Raman peak at ~2000, ~3000 or ~3500 cm\(^{-1}\), characteristic of OH vibrations, and therefore indicative that tsangpoite and matyhte are OH-free [6]. While further thermochemical and kinetics evidences are required to clarify the exact formation mechanisms/conditions of the euhedral tsangpoite, matyhte and kuratite at the grain boundary of angrite D’Orbigny, we favor formation via off-eutectic solidification of the P-rich partial melts/fluids over Fe-sulfide upon cooling. These processes took place at \(T >1000^\circ\)C, considering the 900-1100°C stability field of rhômites (kuratite), and/or the formation of merrillite (matyhte) without whitlockite component, i.e. hydroxyl, at \(T >1050^\circ\)C [e.g. 8]. This metasomatic event must only last for a short time, as shown by the Pb isotopic \(^{206}\)Pb/\(^{207}\)Pb age of the silicophosphates (4568 ± 20 Ma [7]) akin to the ages of the whole rock and mineral phases in D’Orbigny dated with \(^{53}\)Mn-\(^{53}\)Cr and \(^{207}\)Pb/\(^{206}\)Pb methods (4562± 0.6 Ma and 4564.2± 0.12 Ma), respectively [9-10].

Figure 1: SEM-BEI micrographs showing the “intact” FeS at the impinged Fa-Kir overgrowths (a-b). Tsangpoite crystals in residue FeS (c).

Figure 2: SEM-BEI micrographs showing the concurrent presence of (a-d) tsangpoite at the core and matyhite at the rim of resorbed Fe-sulfide (in red envelop), and (e,f) tsangpoite at the core and matyhite at the areas of contact with Fa-Kir overgrowth of a partially altered Fe-sulfide.

Figure 3: a) SEM-BEI micrographs of an oblique tsangpoite crystal nucleated from the FeS crystal with central tube filled by FeS + magnetite + Fe. b) The corresponding TEM image showing Fe-assemble at central tube and the variable Si/P ratios from core to rim of the tsangpoite. c) Association of tsangpoite + kuratite. The two branches of tsangpoite grew around FeS is faceted by \{1100\} an \{1102\} planes.